

Effect of local structural distortions on magnetostructural transformation in Mn_3SnC

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Abstract

In this paper we attempt to understand the different nature of first order magnetic transformation in Mn_3SnC as compared to that in Mn_3GaC . The transformation in Mn_3SnC is close to room temperature ($T_t \approx 280\text{K}$) and is associated with a large change in magnetic entropy that makes it a suitable candidate for applications in ferroic cooling. Using a combination of x-ray and neutron diffraction and x-ray absorption fine structure (XAFS) spectroscopy we infer that the magnetic ground state consisting of antiferromagnetic and ferromagnetic Mn atoms is due to structural distortions present in Mn_6C octahedra.

Keywords: Antiperovskites, magnetostructural transformation, EXAFS, Mn_3SnC

PACS: 75.30.Sg; 61.05.cj; 75.30.Kz

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1. Introduction

Antiperovskite compounds that have attracted considerable attention due to significant properties like superconductivity [1, 2], giant magnetoresistance [3], magnetostriction effect [4] and giant negative thermal expansion (NTE) [5, 6, 7, 8, 9]. Amongst these is Mn_3SnC which exhibits a large magnetic entropy change near room temperature with ΔS_{max} values ($\sim 80.69 \text{ mJ/cm}^3\text{K}$ and $133 \text{ mJ/cm}^3\text{K}$ under a magnetic field of 2T and of 4.8T, respectively) comparable to those observed in contemporary magnetic refrigerant materials [10]. In spite of its relatively simple cubic structure (*Sp. Gr. $Pm\bar{3}m$*) with Mn atoms located at the face centers of a cube, Sn atoms at the corners and carbon atom positioned at the body center [11], Mn_3SnC transforms from a room temperature paramagnetic (PM) state to a high volume magnetically ordered state with a complicated spin arrangement consisting of antiferromagnetic (AFM) and ferromagnetic (FM) components via a spontaneous first order transition at 280K [12, 13, 14, 10]. The non collinearity of Mn spins in the transformed state has been attributed to a novel magnetic structure obtained from neutron diffraction studies. Though equivalent in crystal structure, Mn atoms in the magnetic unit cell $(a\sqrt{2}, a\sqrt{2}, a)$ of Mn_3SnC generated using a propagation vector $k = [\frac{1}{2}, \frac{1}{2}, 0]$ are of two types. Firstly, two of the three Mn atoms present themselves in a square configuration in the (001) plane with a net antiferromagnetic moment of $2.4\mu_B$ per Mn along with a small FM moment of $0.2 \pm 0.15\mu_B$ along the [001] direction. While, the remaining Mn atoms have their spins aligned parallel to each other thus contributing to the FM component with a moment of $0.65 \pm 0.15\mu_B$ along the 001 direction [13]. In contrast, Mn_3GaC , which also undergoes a first order transition at $T \sim 160\text{K}$ has a collinear AFM structure described by a propagation vector $k = [\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$ resulting in ferromagnetic [111] planes of Mn atoms alternating in their spin direction along the (111) axis [15].

2. Experimental

To prepare polycrystalline Mn_3SnC , starting materials (Mn, Sn and C powders) were separately weighed and intimately mixed in the stoichiometric molar ratio 3:1:1 with about 15% excess graphite powder added to compensate possible carbon deficiencies during the reaction [16]. The mixture was then pressed into a pellet and encapsulated in an evacuated quartz tube before sintering at 1073K for the first 48 hours and at 1150K for the next

120 hours [10]. After quenching to room temperature, the product was pulverized, mixed and annealed again under the same conditions to obtain a homogeneous sample. Room temperature x-ray diffraction (XRD) studies were carried out using a Rigaku diffractometer with $\text{CuK}\alpha$ radiation to determine the phase formation and purity of the compound formed. Thermal expansion across the first order transition was measured from XRD patterns recorded in the temperature range of 25-300K using BL18B at Photon Factory, Japan. Temperature dependent magnetization measurements in the 5-300K range were performed using Quantum Design SQUID magnetometer in an applied field of 0.01T while resistivity measurements in the same temperature range were accomplished using standard four probe method. Neutron powder diffraction patterns as a function of temperature were recorded on the PD2 diffractometer ($\lambda = 1.2443\text{\AA}$) at Dhruva reactor, Bhabha Atomic Research Centre, Mumbai, India. Rietveld analysis for all diffraction patterns was performed using the FullProf Suite refinement program [17]. To understand the local structural changes, if any, in the Mn-C octahedra in Mn_3SnC , Extended x-ray absorption fine structure (EXAFS) data at the Mn K edge (6539 eV) was collected in transmission mode at 300K (RT) and 80K (LT) in the range from -200 to 1300 eV with respect to the Mn K edge at the XAFS beamline at Elettra, Trieste [18]. Both incident (I_0) and transmitted (I) intensities were measured simultaneously using an ionization chamber filled with appropriate gases. To restrict the absorption edge jump ($\Delta\mu$) to an optimum value, the number of layers of Mn_3SnC powder coated scotch tape were appropriately adjusted. The edge energy was calibrated using Mn metal foil as standard. To obtain EXAFS ($\chi(k)$) signal, Mn K edge data was reduced following standard procedures in Demeter program [19].

3. Results and Discussion

Room temperature XRD pattern recorded in the angular (2θ) range of 20° to 100° in steps of 0.02° using Cu $\text{K}\alpha$ radiation is presented in Figure 1. Rietveld refinement of the pattern shows the formation of cubic Mn_3SnC with a lattice constant, $a = 3.99672(4)$ [12] along with minor impurities of C, Sn and SnO .

Magnetization (M) measurements recorded as a function of temperature under zero field cooled (ZFC), field cooled cooling (FCC) and field cooled warming (FCW) conditions at an applied field of 0.01T are shown in Figure 2a. The M(T) curves exhibit a sharp increase in magnetization at $T \sim 279$

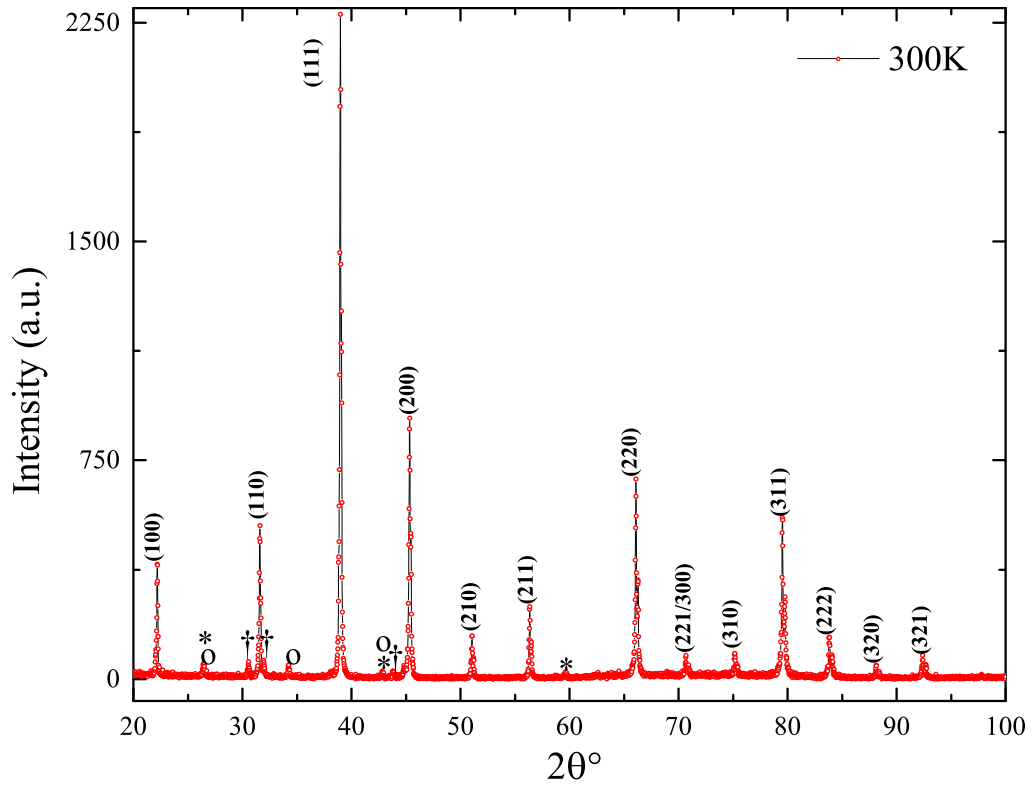


Figure 1: X-ray diffraction pattern recorded for Mn₃SnC at room temperature. “*,†, o” represent minor impurities ($\sim 1\%$) of C, Sn and SnO respectively.

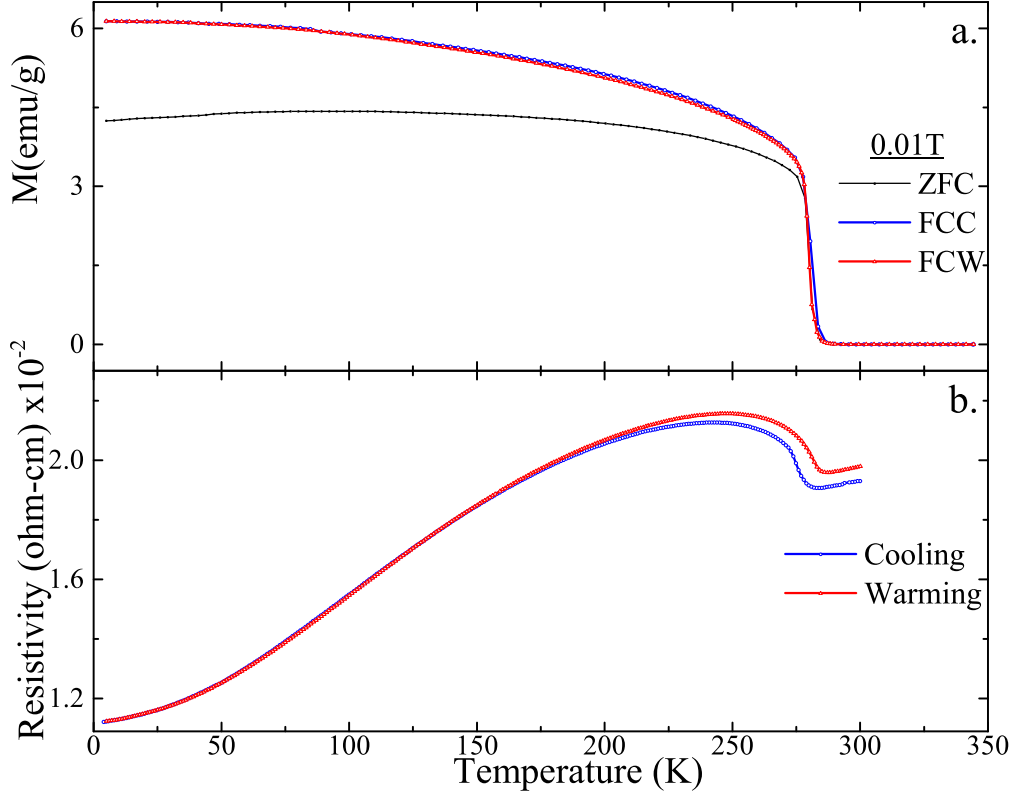


Figure 2: Temperature dependence of a. Magnetization under ZFC, FCC and FCW processes in an applied field of 0.01T and b. Electrical resistivity of Mn_3SnC compound.

K corresponding to a transition from a high temperature PM state to a low temperature magnetically ordered phase with competing FM and AFM interactions [13]. Temperature dependent resistivity plots in Figure 2b measured in zero applied field illustrate that the transport behaviour of Mn_3SnC is metallic across the 5-350K range [10] with a sharp discontinuity in resistance around the Curie temperature ($T_C \sim 279\text{K}$). Existence of thermal hysteresis between the cooling and warming process in both magnetic and transport measurements implies the first order character of the transition at T_C .

X-ray diffraction intensities in the 25-300K temperature range were collected over a 2θ range between 8° - 45° with a step size of 0.005° using an x-ray wavelength $\lambda \sim 0.619\text{\AA}$. Abrupt structural changes that occur around the ordering temperature are highlighted in Figure 3 via the temperature

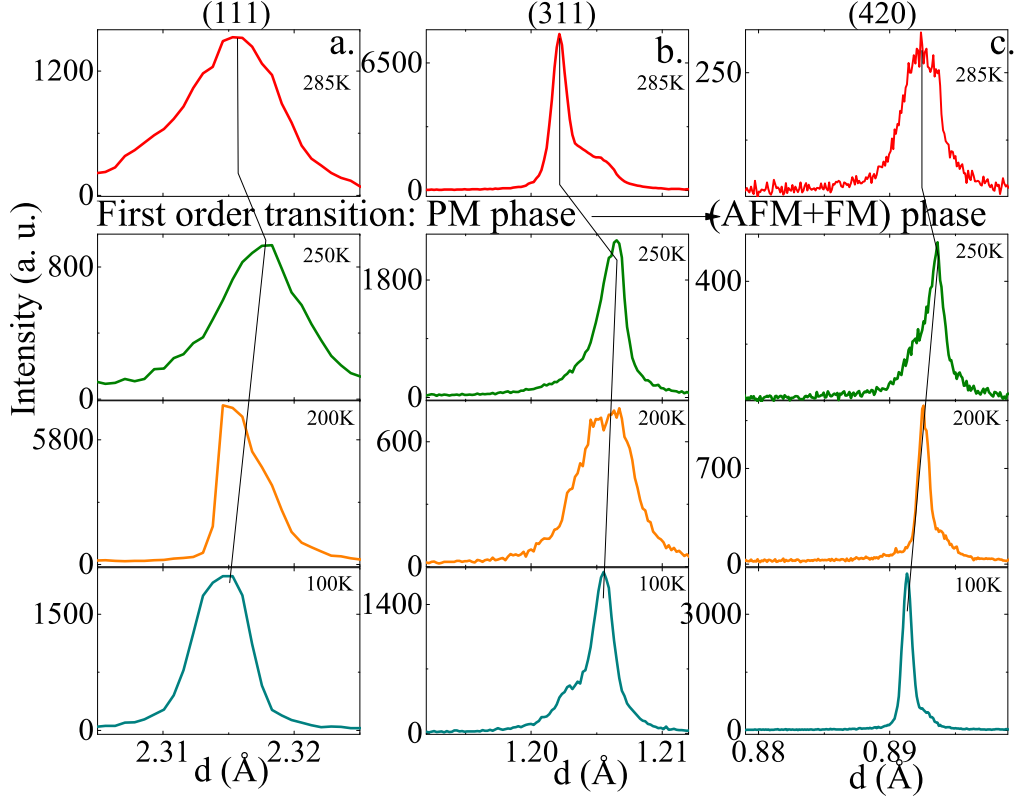


Figure 3: Thermal evolution of the (111), (311) and (420) X-ray reflections across the transformation temperature in Mn_3SnC .

evolution of the (111), (311) and (420) reflections. One can notice a sudden shift in the position of these reflections to higher values of inter planar distance ' d ' between 285K and 250K. This fact coupled with the absence of any additional peak indicates that Mn_3SnC undergoes a cubic-cubic volume discontinuous transition at about 279K along with a change in its magnetic state. The calculated change in the lattice constant value at the transition is of the order of 0.1% which is in agreement with previously reported values [14].

As mentioned before the non collinearity of Mn spins observed in Mn_3SnC below T_C is attributed to a complicated arrangement of FM and AFM spins. To reconfirm magnetic structure below its Curie temperature and to study the thermal evolution of Mn magnetic moments, neutron diffraction pat-

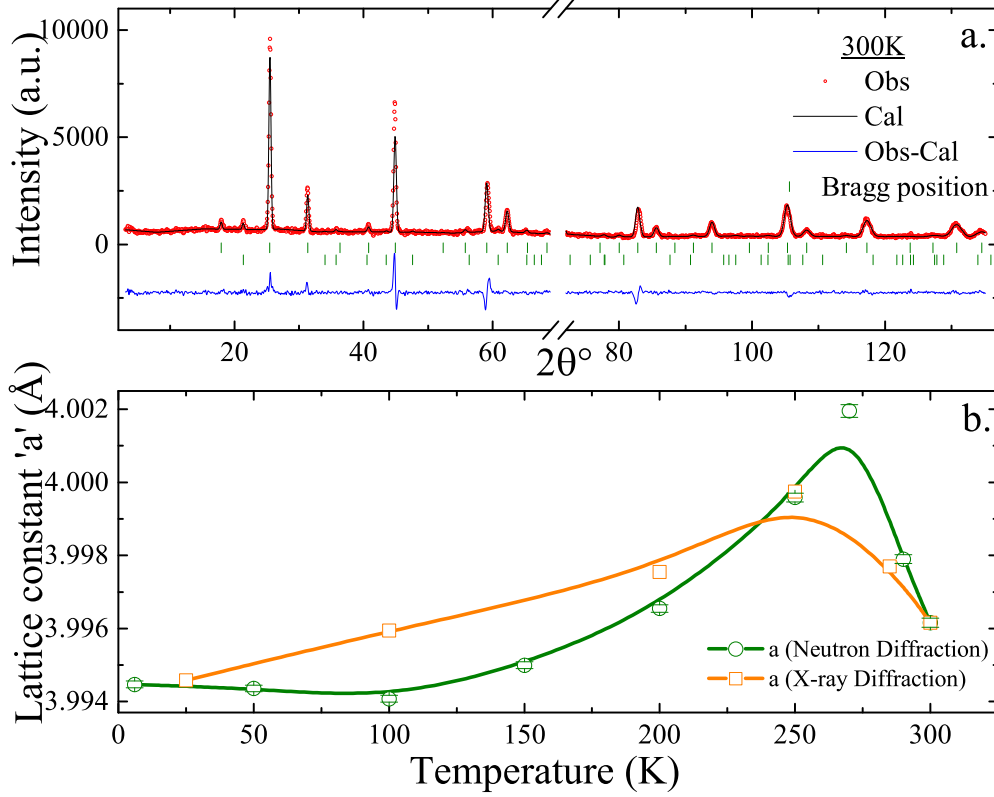


Figure 4: a. Rietveld refined neutron diffraction patterns of Mn_3SnC recorded above the magnetic ordering temperature ($T = 300\text{K}$). b. Variation of refined lattice parameters obtained from neutron diffraction (open circles) and synchrotron x-ray diffraction (open squares) as a function of temperature.

terns were recorded at selected temperatures between 6K and 300K, in the angular range $3^\circ - 135^\circ$. The patterns were Rietveld refined to obtain the crystal and magnetic structure. At 300K, Bragg reflections corresponding only to the nuclear structure (in the space group $\text{Pm}\bar{3}\text{m}$) and impurity phase C are present as can be seen in Figure 4a. The refined value of lattice constant obtained from this fitting ($a = 3.9961(1)\text{\AA}$) is in good agreement with that obtained from x-ray diffraction. Temperature dependance of lattice constant values obtained from synchrotron x-ray diffraction and neutron diffraction are shown in Figure 4b. Both the results, obtained from synchrotron x-ray and neutron diffraction, are in fair agreement with each other.

On cooling below T_C in addition to the nuclear scattering peaks defined by the $\text{Pm}\bar{3}\text{m}$ space group superlattice reflections with significant magnetic contribution appear as shown in the diffraction data recorded at 6K in Figure 6a. These magnetic reflections cannot be indexed on the basis of the obtained chemical structure. They can only be indexed by defining a propagation vector as $k = [\frac{1}{2}, \frac{1}{2}, 0]$ and adopting a larger magnetic unit cell of type $(a\sqrt{2}, a\sqrt{2}, a)$ giving rise to a spin alignment shown in Figure 5. This magnetic structure envisages two magnetic Mn atoms. One, Mn1, has only a FM moment $= 0.7 \pm 0.4\mu_B$ along the 001 axis and the other (Mn2) with only an antiferromagnetic component are arranged in a ‘square configuration’ in the a-b plane with a net moment $= 2.3 \pm 0.1\mu_B$. Thermal evolution of the magnetic moments of the two species of Mn atoms present in the magnetic structure of Mn_3SnC is shown in Figure 6b. With the lowering of temperature below transition temperature one can see a sharp increase in the magnetic moment of Mn2 species which is as expected for a first order transformation. While the moment of Mn1 which contributes purely to the FM component exhibits a comparatively gradual increase. Furthermore, with lowering of temperature, while the magnetic moment of Mn2 continuously increases, that of Mn1 shows a slight decrease. The behaviour of Mn magnetic moments near transition temperature, gives an impression that only Mn2 atoms contribute to the first order transformation in Mn_3SnC . Eventhough, magnetic structure has a tetragonal symmetry, no structural distortions were visible either in neutron diffraction or in synchrotron XRD measurements at lower temperatures.

To check the possibility of existence of any local structural distortions around Mn in Mn_3SnC which could be responsible for the above behaviour of Mn spins, EXAFS data recorded at the Mn K edge at RT and LT was analyzed. For this $\chi(k)$ signal in the range 2\AA^{-1} to 13\AA^{-1} was Fourier transformed (FT) to R space. The magnitude of FT of EXAFS data at the two temperatures in the R range of 0 to 6 \AA are presented in Figure 7. The plot shows two distinct peaks between 1 \AA to 3 \AA corresponding to Mn-C and equidistant Mn-Mn and Mn-Sn correlations. The scattering contributions from each of these correlations were obtained using FEFF6.01 [20] and were used in fitting the experimental data in R space in the range 1 \AA to 3 \AA . Since the observed crystal structure at RT is cubic, the data was initially fitted using the structural restrictions imposed by the $\text{Pm}\bar{3}\text{m}$ space group. These restrictions implied that nearest neighbour Mn-C correlation had a

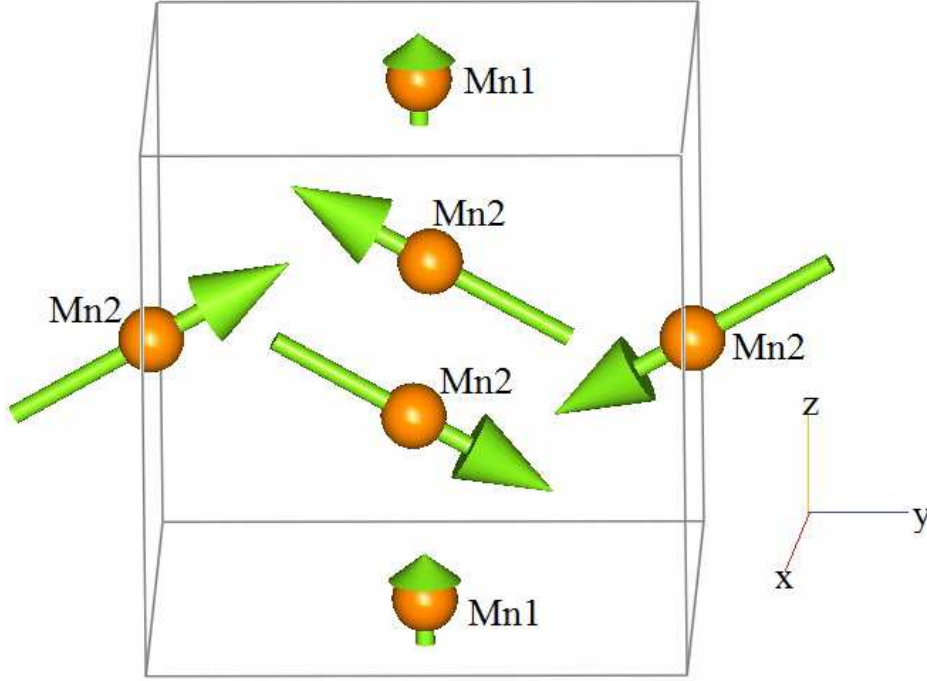


Figure 5: Magnetic spin alignment of Mn atoms in nuclear unit cell of Mn₃SnC at low temperature as obtained from neutron diffraction.

bond distance equal to $a/2 = 1.998\text{\AA}$ and both eight neighboured Mn-Mn and four neighboured Mn-Sn correlations had a bond distance equal to $a/\sqrt{2} = 2.826\text{\AA}$. The resulting fit in the R space and the back transformed k space is shown in Figure 7a. As can be seen, the fit was not quite good (R-factor = 0.04720). An attempt to fit the data by relaxing the above restrictions resulted in a very good fit. However, Mn-Mn bond length was obtained to be slightly shorter than Mn-Sn bond distance. This hints towards the presence of local structural distortions. Taking into account the crystal and magnetic structure obtained from x-ray and neutron diffraction a model was designed consisting of a fraction ' x ' of shorter and longer bond distances of Mn with its near neighbours while still preserving the structural restrictions imposed by the crystal structure. Such a model resulted in a very good fit (R-factor = 0.01399), (see Figure 7c) wherein about two third of the nearest neighbour Mn-C distances are shorter while the remaining one third are

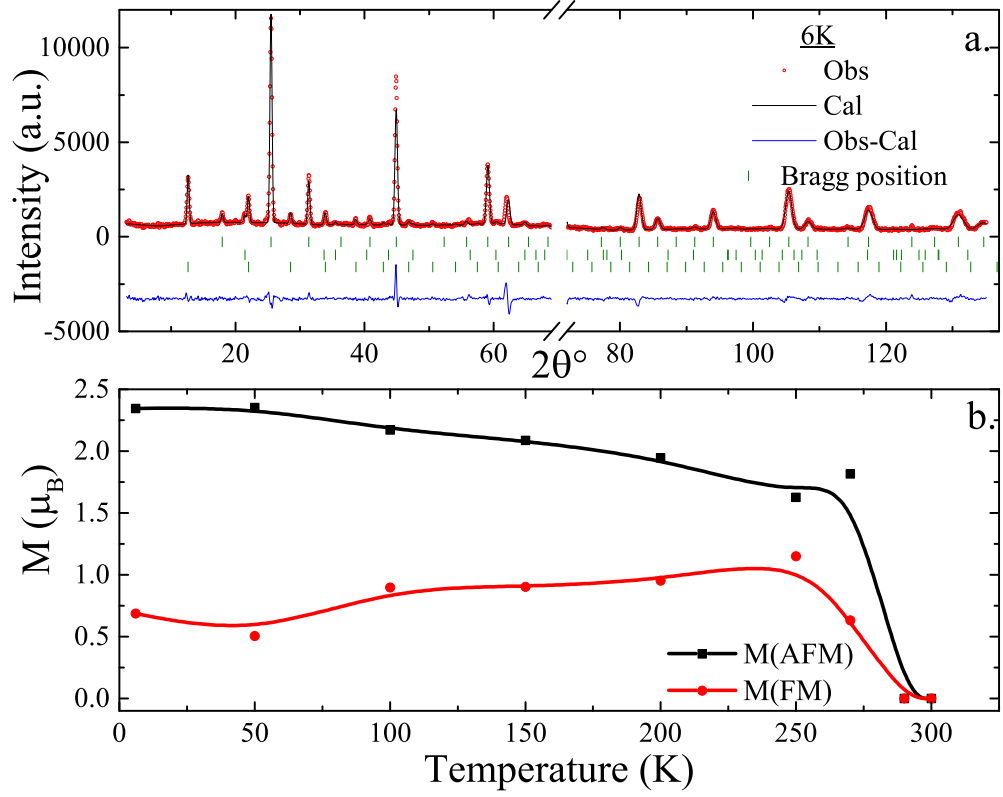


Figure 6: a. Rietveld refined neutron diffraction patterns of Mn_3SnC recorded below the magnetic ordering temperature ($T = 6\text{K}$). b. Variation of refined magnetic moments of the two species of Mn atoms in Mn_3SnC magnetic structure as a function of temperature.

Table 1: Interatomic bond distance R and mean-square displacement of the path lengths due to thermal or static disorder ' σ^2 ' obtained for Mn_3SnC compound by fitting Mn K-edge EXAFS to a model representing distorted octahedra. C.N. corresponds to the coordination number, $R_{300\text{K}}$ and $R_{100\text{K}}$ are interatomic distances calculated from neutron diffraction pattern at 300K and 100K respectively, ' x ' denotes the fraction of elongated/shortened bond lengths).

Bond	C.N.	$R_{300\text{K}}(\text{\AA})$	x	RT		$R_{100\text{K}}(\text{\AA})$	x	LT	
				$R(\text{\AA})$	$\sigma^2(\text{\AA}^2)$			$R(\text{\AA})$	$\sigma^2(\text{\AA}^2)$
Mn-C	2	1.998	0.37(3)	2.032(2)	0.006(3)	1.997	0.32(4)	2.029(3)	0.009(5)
			0.63(3)	1.958(2)			0.68(4)	1.961(3)	
Mn-Mn	8	2.826	0.37(3)	2.874(2)	0.006(1)	2.824	0.32(4)	2.869(3)	0.005(1)
			0.63(3)	2.769(2)			0.68(4)	2.773(3)	
Mn-Sn	4	2.826	0.37(3)	2.769(2)	0.008(1)	2.824	0.32(4)	2.773(3)	0.006(1)
			0.63(3)	2.874(2)			0.68(4)	2.869(3)	

longer. Likewise around two third Mn-Mn distances and about one third of Mn-Sn distances were found to be shorter and the remaining fraction longer. Such a fitting indicates that Mn_6C octahedra distort from their cubic symmetry by elongating along one direction and shrinking along the other two. The structural parameters obtained from the fitting are tabulated in Table 1. The same model can also be used to fit the LT data equally well but with shorter bonds showing a small increase in their bond lengths and the longer bond distances reducing in their lengths.

Even though no structural disorder is seen in room temperature x-ray or neutron diffraction patterns of Mn_3SnC , EXAFS analysis indicate a presence of local structural disorder around Mn atoms in the paramagnetic phase. The presence of such a distortion at RT in Mn_3SnC could be either due to the proximity to the magnetostructural transition temperature or due to the presence of larger atom like Sn. It may be mentioned here that such local structural distortions have not been hitherto reported in other antiperovskite compounds above their transformation temperature. Larger atoms like Sn could induce local strains which may be alleviated by a structural distortions while maintaining the cubic symmetry of the overall crystal structure. EXAFS studies also show that though distortions persist even in the magnetically ordered phase the shorter bond distances tend to elongate while the longer bond distances shrink.

The presence of such a disorder could also be the reason behind the change

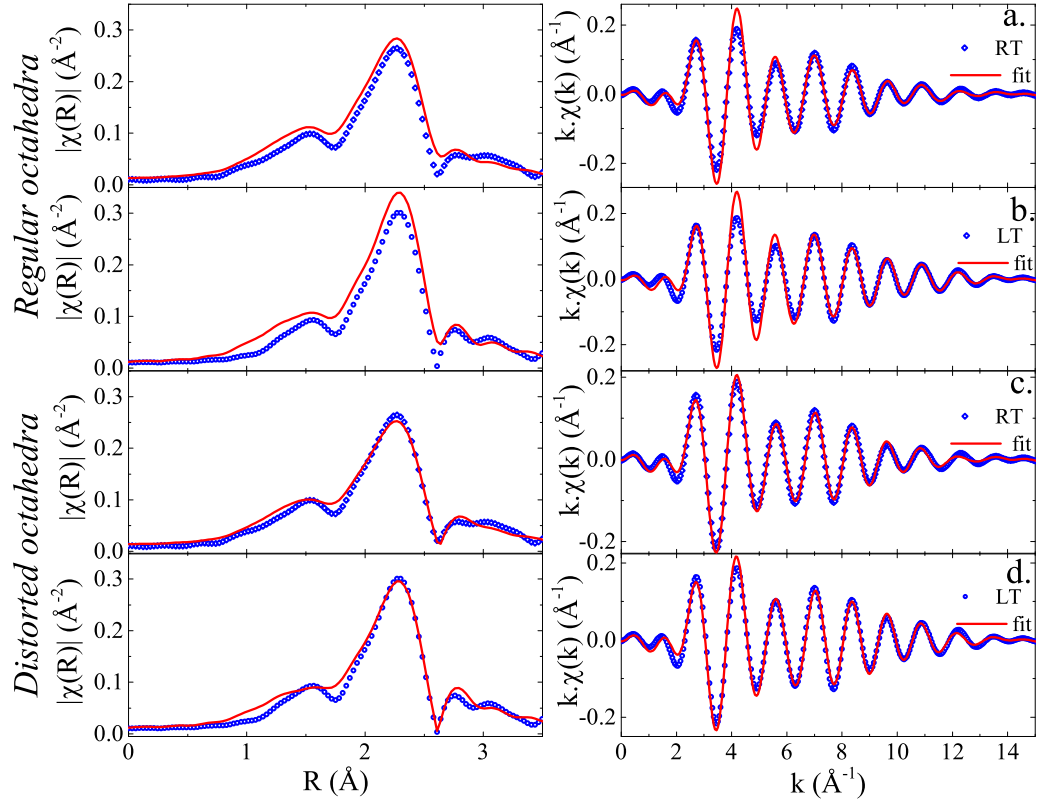


Figure 7: Comparison between fitted FT Mn K-edge EXAFS data recorded for Mn_3SnC at RT and LT using the two structural models.

in magnetic propagation vector from $(0.5, 0.5, 0.5)$ in Mn_3GaC to $(0.5, 0.5, 0)$ in Mn_3SnC . It is known that in antiperovskites, the nature of magnetic order critically depends on the competition between the interaction strengths of Mn–Mn nearest neighbour J_1 and next nearest neighbour J_2 interactions which are of opposite sign. The frustration caused due to this competition is often alleviated by a structural transformation. In the case of Mn_3SnC , the presence of a local structural distortions could be the reason for its unusual magnetic ground state.

4. Conclusions

A systematic exploration of the Mn_3SnC crystal structure using a combination of x-ray and neutron diffraction and x-ray absorption fine structure (XAFS) spectroscopy was carried out to understand the nature of the first order magnetic transformation in the compound. Although x-ray and neutron diffraction patterns show no structural distortions in the compound at low temperatures, they indicate a cubic-cubic volume discontinuous transition accompanying the magnetic transition ($T \sim 279\text{K}$). However EXAFS results suggest a structural distortion of the Mn_6C octahedra from their cubic symmetry due to presence of larger atoms of Sn. These distortions critically affect the magnetic order of Mn_3SnC ground state consisting of antiferromagnetic and ferromagnetic Mn atoms.

Acknowledgments

This work is supported by Board of Research in Nuclear Sciences (BRNS) under the project 2011/37P/06. Further financial support and experimental facilitation granted by Department of Science and Technology, India and Saha Institute of Nuclear Physics, India at the Indian Beamline, Photon Factory, KEK, Japan is gratefully acknowledged. M/s Devendra D. Buddhikot, Ganesh Jangam and Dr. V. Srihari are acknowledged for the experimental assistance.

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